Properties of Novel Liquid Crystalline Thermosets Oriented by Magnetic Fields

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Liquid crystalline thermosets (LCTs) are low molecular mass liquid crystals with cross-linking groups attached. They can be cross-linked thermally, chemically, or photochemically, maintaining the liquid crystalline order. LCTs have a number of outstanding properties, including high fracture toughness and low permeability to moisture. The liquid crystalline structure also allows bulk orientation in high magnetic fields due to the molecular anisotropy of the diamagnetic susceptibility. This orientation leads to improved properties, such as high tensile modulus.

To prepare samples, the monomer was melted and the curing agent (2,4-diaminotoluene, or DAT) was thoroughly dissolved in the melt. The melt was poured into a heated aluminum mold and kept in the freezer until use to prevent further reaction. Curing was conducted in the 195 mm, 20 T magnet at the NHMFL; curing was conducted in the magnet at either 150° or 160° C for one hour. After magnetic field processing the curing was completed in a conventional oven.

Mechanical properties were measured using dynamic mechanical analysis (DMA) in a three point bend geometry. Tab. 1 shows the DMA results.

From these data, it can be seen that the glass transition and activation energy for the glass transition are unaffected by the magnetic field. This result is consistent with our previous results. Surprisingly, the modulus appears to decrease with increasing field strength; this is opposite to the expected trend. We are currently performing x-ray measurements to quantify the degree of orientation in these samples to understand this result.

Table 1. DMA values.

Magnetic Field (T)	Modulus at 25°C(10^9Pa)	Glass Transition(°C)	Activation Energy for Glass Transition(kJmol)
0	4.48	93	697
7	1.80	91	645
15	1.40	93	674

In this study, our intention was to expand the number of LCTs that have been oriented in magnetic fields, and to determine how changes in molecular structure and liquid crystalline phase may affect their ability to be oriented. To that end, a series of novel LCTs with azomethine mesogens and epoxy end groups were synthesized.

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High Temperature Texturing of Ne-Fe-B

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Texturing of crystalline materials under an externally applied magnetic field is an important process in many fields of materials science.[1] Heat treatment can be done at a certain temperature range in field, rather than at prolonged annealing, to produce a dominant crystalline orientation. A fundamental research of the effect of magnetic field on the texturing process has been initiated and applied to a number of materials systems. Here, we report on the texturing of $Ne_2Fe_{14}B$ at high temperature with an applied field.

Using a prototype furnace, a 1 x 1 cm^2 of $Ne_2Fe_{14}B$ (tetragonal structure) was annealed at 1200° C for 3 hours under argon without an applied field. X-ray diffraction (XRD) 2Θ/Θ scan showed a decrease in texture compared to the as-received materials (Fig.1).

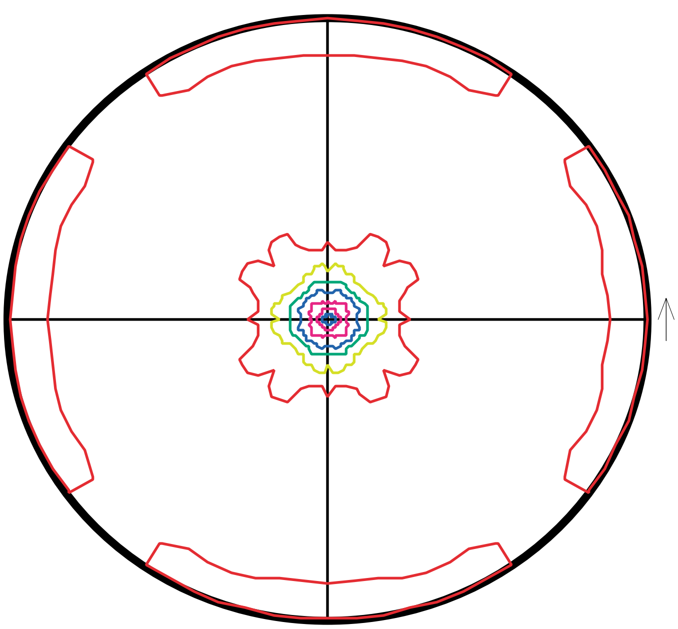

Figure 1. Calculated (001) pole figure for the as received material.

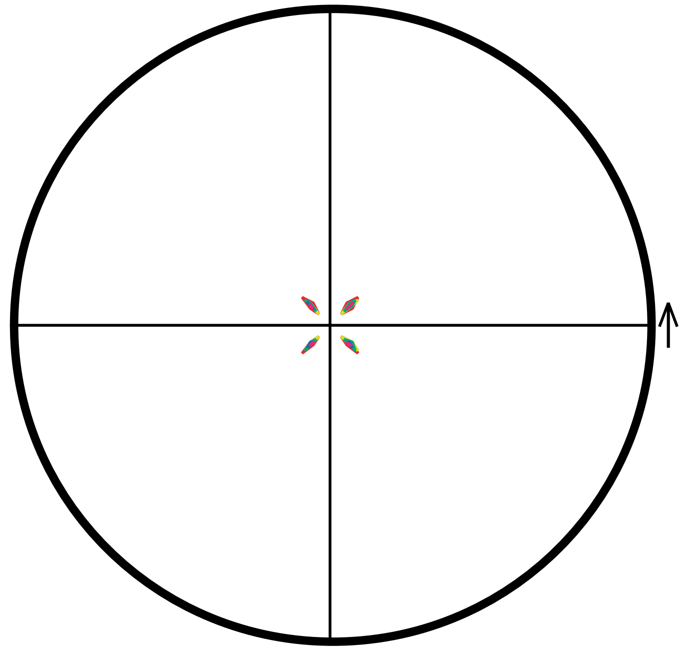

Figure 2. Calculated (001) pole figure for the thermomagnetically annealed material.

Using a new sample with the same size, the experiment was repeated under the same conditions, except this time under a field of 8 T. XRD 2Θ/Θ scan showed an increase in crystallinity. Fig. 2 shows that the material is textured. As can be seen from the pole figure, the c-axis orientation is tilted to about 10° from the normal.

$Ne_2Fe_{14}B$ annealed without field has a random texture; whereas, when annealed under an applied field, a preferred orientation is produced.

Acknowledgements: The authors would like to thank Prof. Shahin for providing us with the samples.

[1] Tournier, R., *et al.*, Nature, **349,** 770 (1991).

Development of Cobalt-Based Alloy Strengthened by Nanoscale Structure

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The limits and durability of a high strength cobalt-based alloy, MP35N (nominal composition in wt% is 35%Co-35%Ni-20%Cr-10%Mo), were studied and related to the phase transformation and atomistic structure of the alloy in order to expand its limits. The study leads to an alloy with unmatchable and versatile mechanical properties achieved by optimized cold deformation and heat treatment. The alloy is being used as reinforcement for various magnets and pressure vessels for testing materials in a magnetic field. The optimized properties of this cobalt-based alloy provide an opportunity to achieve higher magnetic field in various magnets.

The limit of the cobalt-based alloys is its achievable strength in large heat in a repeatable manner. Therefore, the research and development were undertaken in collaboration with industrial partners.

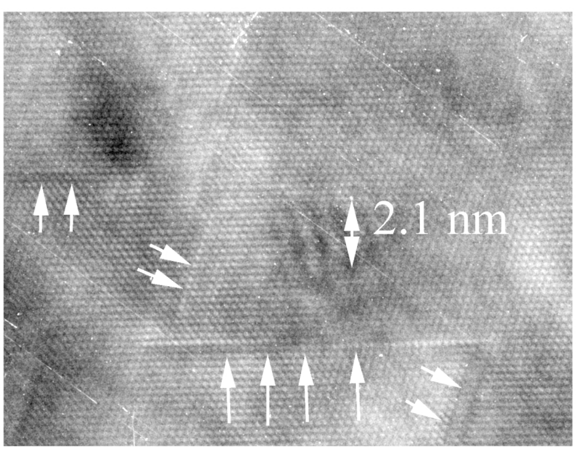

Figure 1. Transmission electron microscopy image in atomic resolution of MP35N rolled to 65% and aged at 866 K for 64 hours showing the precipitates or planar defects indicated by arrows on {111} planes of fcc matrix. The contrast differences in these regions indicate the alloy element segregation.

At a large deformation strain achieved by rolling, twins and stacking faults form in metastable face-centered-cubic matrix of this cobalt-based alloy. The stacking faults and twins are only one or two atomic layers thick. Because of the segregation of the atoms to those sites, nanometer second phase forms. The formation of twins or stacking fault platelets during deformation can strengthen the material in a variety of ways. The production of interfaces or twin boundaries may provide additional barriers to plastic flow, and hence strengthen the materials. The dislocation structure accumulated prior to twinning and formed by subsequent deformation may in part be transformed to sessile dislocations, and hence harden the material.

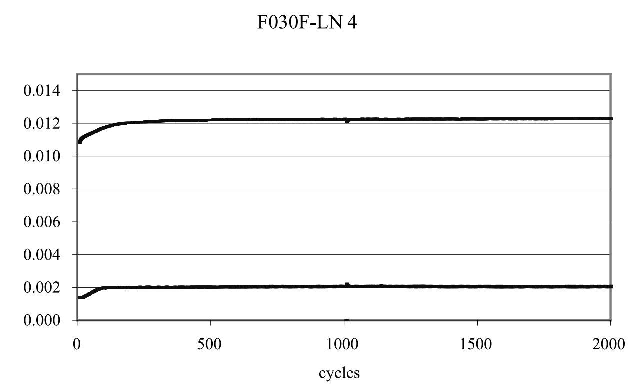

Figure 2. The strain variations of MP35N rolled to 65% reduction-in-area and aged at optimized heat treatment conditions showing that no further plastic deformation occurs after about 500 cycles. The cyclic tests were done at 77 K.

The strengthening of MP35N by aging occurs only after cold-working and is attributed to further segregation of the solute atoms to the stacking faults and twins or formation of extremely fine precipitates (about a few atomic layers thick) with hexagonal crystallographic structure, as shown in Fig. 1. The habit planes of the precipitates are {111} type. The aging also results in the lattice parameter changes in fcc matrix.

The optimized distributions of the planar defects and precipitates achieved by current deformation and heat treatment procedures ensure a strength level of 2500 MPa at 77 K in this alloy. The alloy can sustain a cyclic-stress-amplitude of 2200 MPa for 2000 cycles without fracture (Fig. 2) and meets the current design requirement for 100 T non-destructive pulse magnet insert.

Magnetically Induced Planar Grain Boundary Motion in Zinc Bicrystals

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Macroscopically, a grain boundary (GB) represents an interface between two differently oriented crystals (grains) in a single phase material. At elevated temperatures, these interfaces become increasingly mobile due to thermal activation. Throughout different GBs, the mobility (a proportionality factor between velocity and driving force) is not uniform by far. An insight into the behavior of individual GBs is therefore of fundamental importance for a profound understanding of technological relevant processes like recrystallization and grain growth. For this purpose, the motion of planar GBs was studied in samples containing one particular type of GB (bicrystals).

Thermodynamically, a driving force for GB motion is given by a reduction of the system's total free Gibbs energy due to this very motion. In deformation free (thus dislocation poor) pure metals, this is the case if either the total GB area is reduced or if individual grains contribute differently to the total energy by a growth of "low energy" grains at the expense of "high energy" grains. The latter case allows it to study planar GBs. It can be achieved through the interaction of a uniform external field with an anisotropic property of the material in question. In the present investigation, this was done by annealing specially grown bicrystals of (dia)magnetic anisotropic zinc in a magnetic field. According to Mullins,[1] the driving force p, depends only on the asymmetry of the spatial orientation of both grains with respect to the magnetic field, the absolute size of the magnetic field strength H, and the anisotropy of the material's susceptibility $\Delta\chi$:

$$p = \mu_0 \frac{\Delta\chi}{2} H^2 (\cos^2 \theta_1 - \cos^2 \theta_2) \qquad (1)$$

With θ_i for the angle of the c-axis of grain i with respect to the magnetic field, and μ_0 for the magnetic field constant. Thus, approximately, with a magnetic field strength of 20 MA/m and a difference in volume susceptibility of 0.5 10^{-5}, a driving force of up to 1.3 KJ/m^3 is feasible. Furthermore, it is known from literature,[2] as well as from our measurements, that the maximum difference of the magnetic susceptibility remains virtually constant up to temperatures near the melting point.*

Figure 1. Former (left) and current (right) position of a GB after a 1140s anneal at 405° C and 19.9 MA/m. The macroscopic GB shape indicates that it was hindered at the upper sample edge. The boundary displacement on the opposite side was less pronounced.

Subject of the current investigation was a 86.0° $\langle 11\bar{2}0 \rangle$ symmetrical tilt GB ($\Sigma 15$)[3] in high purity zinc (99.99+%). This boundary was chosen because it combined a near perpendicular misorientation angle (enabling a maximal driving force) with a CSL coincidence. A number of bicrystalline samples (18x4x2mm^3) were prepared with a misorientation in the vicinity of this special boundary. Finally, these samples were annealed in a maximum driving force position at approximately 25 T, high homologue temperatures, and in a protective atmosphere of high purity argon. Grain boundary motion was measured discontinuously by optical microscopy, utilizing the polarizing effect of zinc on visible light.

The results evaluated thus far showed the following.

(1) The magnetic anisotropy in zinc is well enough pronounced to drive planar GBs in magnetic fields of attainable strength. This is illustrated in Fig. 1, which shows the displacement of a GB due to annealing in a magnetic field.

(2) Moreover, very mobile "new" GBs were observed. They covered in the same time window a clearly larger distance than the specially prepared GBs. Furthermore, the results indicate that the new grains, involved with the formation of these new GBs, descend from the sample tips. Nevertheless, from a thermodynamical point of view, their origin still remains obscure. A first analysis reveals that they all share a common feature; a low energy orientation with respect to the magnetic field. A phenomenon which definitely needs to be investigated more thoroughly.

* Up to 4 MA/m it is also practically independent of the field strength.

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1 Mullins, W.W., Acta Met., **4**, 421-432, (1956).

2 Marcus, J.A., Phys. Review, **76**, 413-416, (1949).

3 Bruggeman, G.A., *et al.*, The Nature and Behavior of Grain Boundaries, Plenum Press, **83-122**, (1972).

Influence of Cryogenic Rolling on Microhardness of Dispersion Strengthened Copper IHRP

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Oxide dispersion strengthened copper, which possesses a unique combination of high strength, high electrical and thermal conductivities, appears to be promising for fabrication of Bitter magnet disks. The materials are strengthened by nano-size Al_2O_3 particles and can be further strengthened by work hardening. It is known that the strength of these disks can limit the capacity of resistive magnets. Therefore, the development of novel methods improving these materials is important for the progress in design of new high field magnets.

The objective of this investigation was to determine the relationship between the deformation strain and microhardness of composite C15715 (Cu+0.3wt% Al_2O_3) after rolling at temperatures close to 77 K and room temperature. The initial thickness of the material was 9.4 mm. It has a copper cladding with thickness equal to ~0.4 mm. The average reduction after each rolling pass was 3.9%. Materials were rolled almost up to 65% of total reduction.

Fig. 1 shows a spatial distribution of microhardness across the thickness of the Cu+0.3wt% Al_2O_3 plate. There is a marked difference in microhardness between copper layers and in the Cu+0.3wt% Al_2O_3 part of the plate. At the same time, there is a uniform distribution of hardness within the Cu+0.3wt% Al_2O_3 portion of the plate.

Fig. 2 demonstrates a sharp increase of microhardness during the first 10% of reduction for both temperatures. After 10% of reduction, the microhardness increases much more slowly at cryogenic rolling and decreases at room temperature rolling. For cryogenic rolling, the maximum microhardness (HV=161 kg/mm^2) was reached at about a 42% reduction-in-area. Further

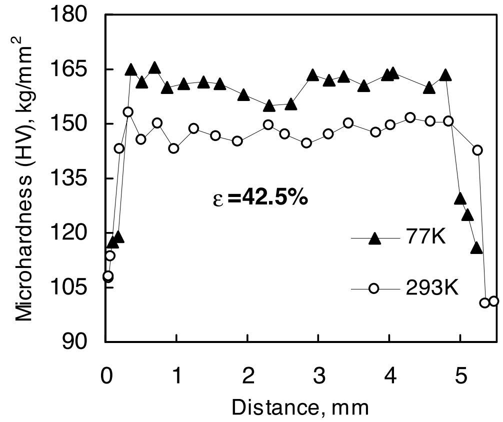

Figure 1. Vickers microhardness (HV, kg/mm^2) as a function of distance across the thickness after 42.5% reduction.

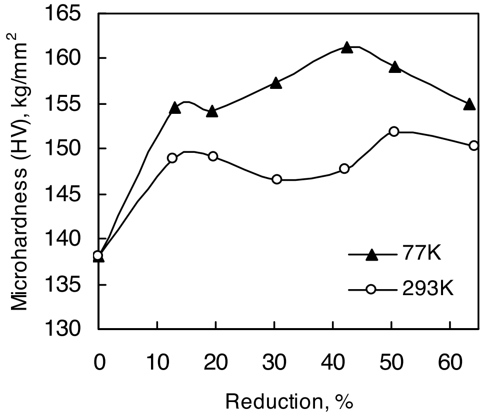

Figure 2. Vickers microhardness (HV, kg/mm^2) as a function of reduction.

rolling decreases microhardness. Rolling at room temperature results in maximal microhardness of HV=151 kg/mm^2 at 57% strain. Remarkably, further increase of reduction decreases the difference in microhardness for rolling at two temperatures.

Thus, for cryogenic rolling, an optimal reduction exists at which the maximum microhardness can be achieved. Further characterization on the strength of the materials achievable by cryogenic deformation is required.

Low Temperature Tensile and Fracture Characteristics of High Purity Niobium

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A study of high purity niobium has been performed at NHMFL/FSU in support of the Accelerator Production of Tritium (APT) project at LANL. Tensile tests at 295, 77, and 4 K and fracture toughness tests at 4 K were performed to characterize the materials. Microstructural and fractographic analyses were also conducted to help evaluate the materials. The materials studied have Nb concentrations ranging from 99.90 wt.% to 99.96 wt. % Nb.

Materials having body-centered-cubic (BCC) crystal structure such as niobium are known to undergo ductile to brittle transitions making them undesirable for cryogenic applications. The chief factors that influence the ductile to brittle transition in BCC metals are stress state, temperature and strain rate. As the temperature is lowered, the lattice resistance to slip progressively increases until at some point the fracture strength may be reached before slip can occur. As a result cleavage or brittle fracture is common in BCC materials at low temperatures.

The 4 K strengths of Nb are about 10 times the 295 K yield and tensile strengths as can be seen

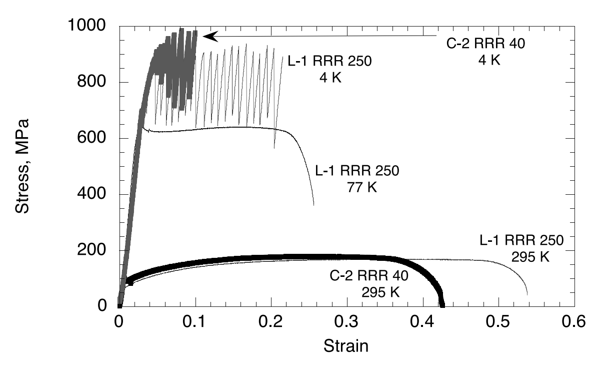

Figure 1. Typical stress vs. strain curves of Nb at the three test temperatures.

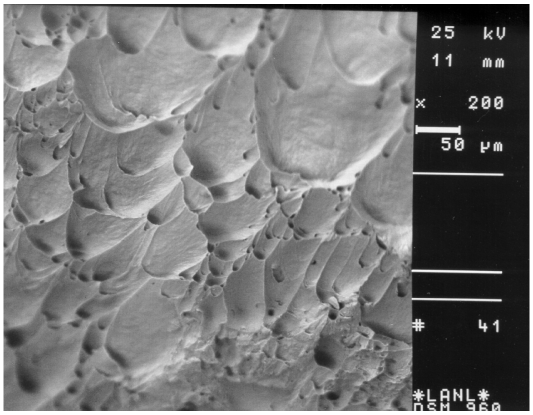

Figure 2A. SEM photograph of L-1 tensile 4 K fracture surface.

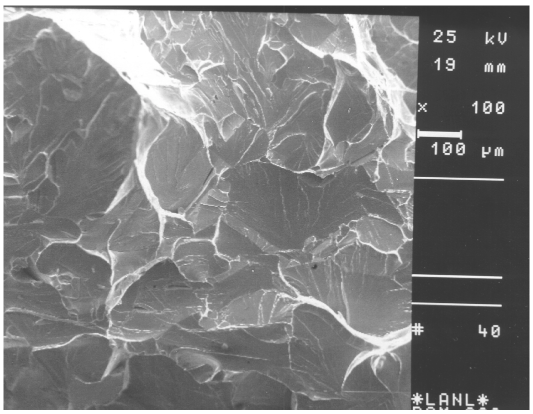

Figure 2B. SEM photograph of L-2 tensile 4 K fracture surface.

in the stress-strain curves (Fig. 1) for two grades (L1 and C2) of Nb with slightly different levels of purity. Over the same temperature range the ductility decreases at least 50 %. The higher purity material L-1 exhibits a clean fracture at 45 degrees to the tensile axis, which is a fracture process attributed to shear stress. The lower purity material C-2 has features of brittle fracture at 4 K, where tensile stress initiates the transgranular cleavage fracture perpendicular to the tensile axis. Higher magnification of the 4 K fracture surfaces of L-1 and C-2 are shown in SEM Fig. 2A and 2B. Here the ductile dimple rupture of material L-1 is in sharp contrast to the brittle cleavage fracture of material C-2. The C-2 material has a considerably higher interstitial content and a smaller grain size. Both the grain size and interstitial content contribute to the higher strength of the C-2 material.

The change in fracture morphology is important with respect to the materials fracture toughness (resistance to fracture in the presence of a flaw) properties. The ductile fracture process is characteristic of high fracture toughness while the brittle cleavage fracture relates to low fracture toughness. High fracture toughness materials are more desirable because they increasing the reliability of the low temperature machine.